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XVII. On the Conversion of a Mixture of dephlogisticated and phlogisticated Air into nitrous Acid, by the electric Spark. By Henry Cavendish, Esq. F. R. S. and A. S.

Read April 17, 1788.

In Volume LXXV. of the Philosophical Transactions, p. 372. I related an experiment, which shewed, that by passing repeated electric sparks through a mixture of atmospheric and dephlogisticated air, confined in a bent glass tube by columns of soap-lees and quicksilver, the air was converted into nitrous acid, which united to the soap-lees and formed nitre. But as this experiment has since been tried by some persons of distinguished ability in such pursuits without success, I thought it right to take some measures to authenticate the truth of it. For this purpose, I requested Mr. GILPIN, Clerk of the Royal Society, to repeat the experiment, and desired some of the Gentlemen most conversant with these subjects to be present at putting the materials together, and at the examination of the produce.

This laborious experiment Mr. GILPIN was fo good as to undertake. It was performed in the fame manner, and with the fame apparatus, which was used in my own experiments, and which is described in the beginning of the above-mentioned Paper, and is accompanied with a drawing. The N n 2 method

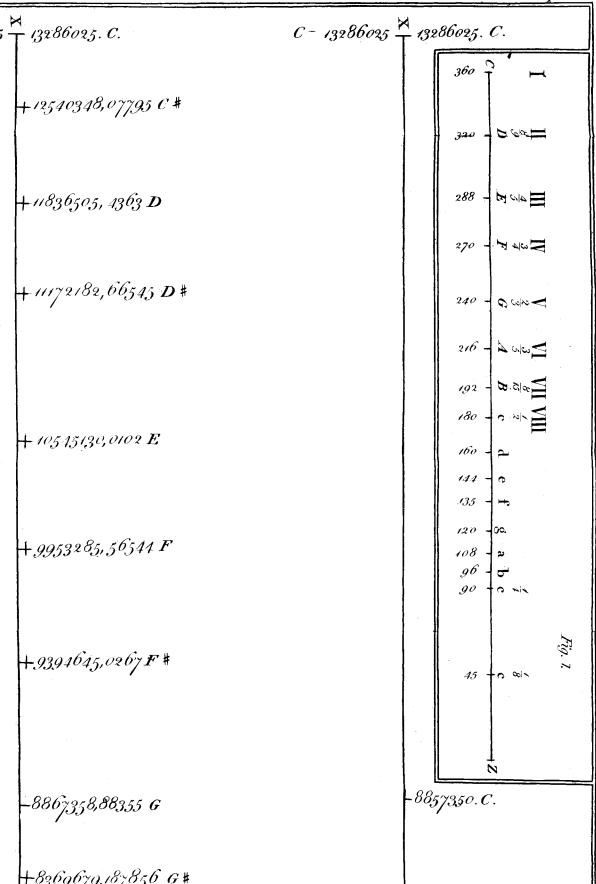
method used for introducing air into the bent tube, was that described in the last paragraph of p. 373. in that Paper, by means of the apparatus represented in fig. 3. or the reservoir, as I shall call it. The soap lees, like those of my own experiments, were prepared from salt of tartar, and were of such strength as to yield $\frac{1}{100}$ of their weight of nitre when saturated with nitrous acid. The dephlogisticated air was prepared from turbith mineral, and seemed by the nitrous test to contain about $\frac{1}{100}$ part of phlogisticated air.

On December 6, 1787, in the presence of Sir Joseph BANKS, Dr. BLAGDEN, Dr. DOLLFUSS, Dr. FORDYCE, Dr. I. HUNTER, and Mr. MACIE, the materials were put together. The quantity of foap-lees, introduced into the bent tube, was 180 measures, each of which contained one grain of quickfilver; and, as the bore of the tube was rather more than one-third of an inch in diameter, it formed a column of five or fix-tenths of an inch in length, which, by the introduction of the air, was divided into two parts, one resting on the quickfilver in one leg of the tube, and the other on that in the other leg. The dephlogisticated air was mixed with onethird part of its bulk of atmospheric air of the room in a separate jar, and the refervoir was filled with the mixture; and from thence Mr. GILPIN, as occasion required, forced air into the bent tube, to supply the place of that absorbed by means of the electric spark.

From what has been faid, it appears, that the mixture employed contained a less proportion of common air than that used in either of my experiments. This made it necessary for Mr. Gilpin now and then to introduce some common air by

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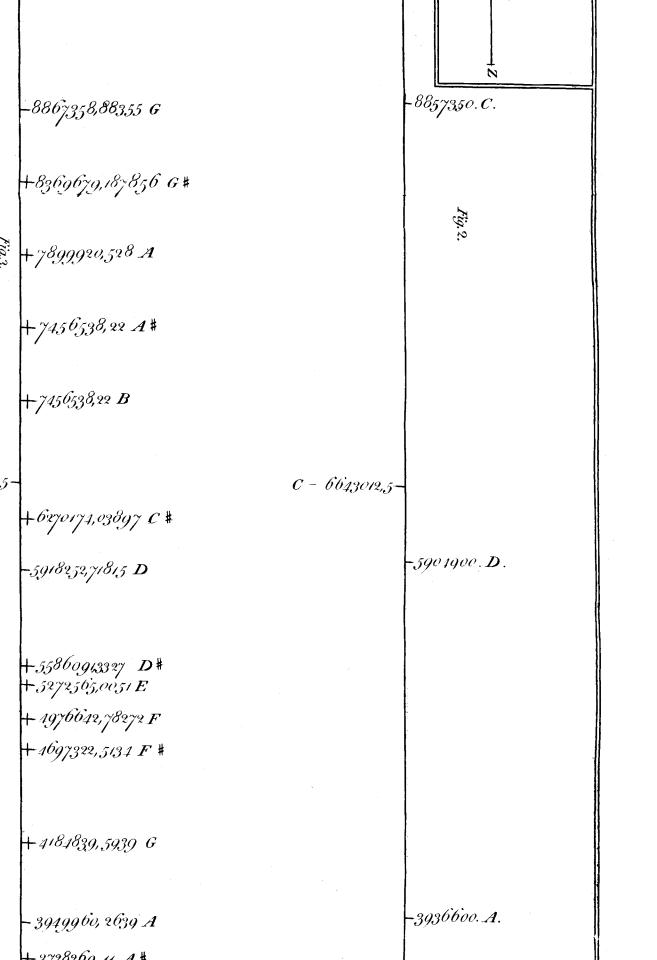
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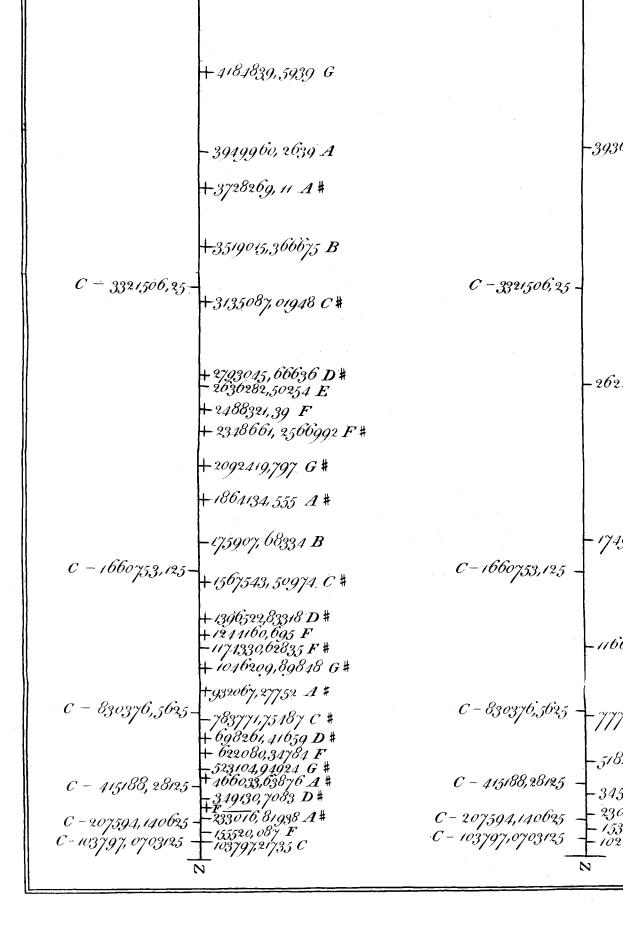
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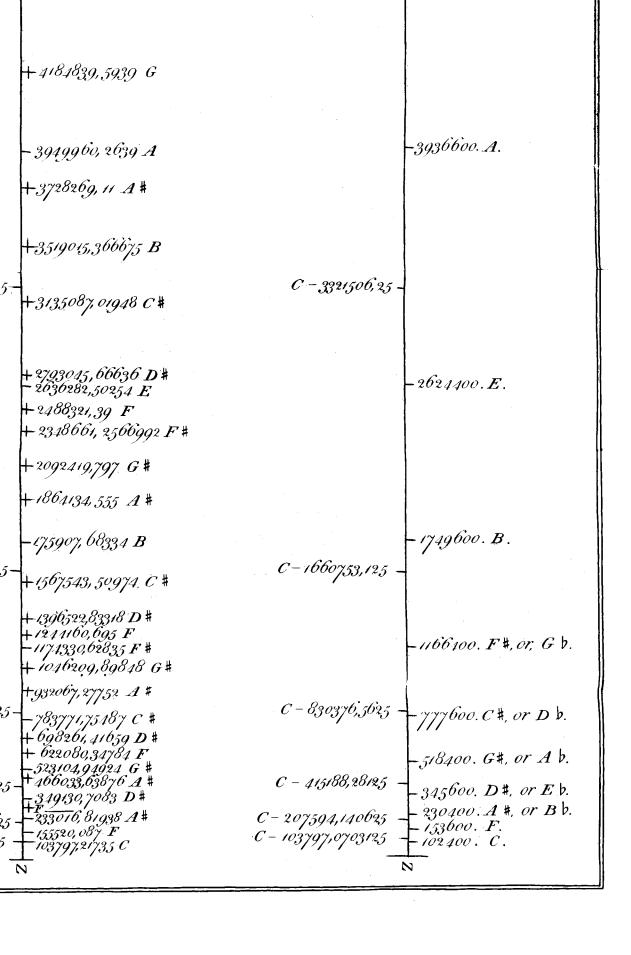
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means of the bent tube represented in fig. 3. of the abovementioned Paper, whenever from the slowness of the absorption he thought there was too small a proportion of phlogisticated air in the tube.

My reason for this manner of proceeding was, that as my first experiment seemed to shew, that the dephlogisticated air ought to be in a rather greater proportion to the phlogisticated than the latter did, I was somewhat uncertain as to the proper quantities, and doubted whether I could proportion them in such manner as that it should not be necessary, during the course of the experiment, to add either dephlogisticated or common air. I therefore mixed the airs in such proportion, that I was sure there could be no occasion to add the former; since it was much easier, as well as more unexceptionable, to add common air than dephlogisticated air.

On December 24, as the air in the refervoir was almost all used, this apparatus was again filled in the presence of most of the above-mentioned Gentlemen, with a mixture of the same dephlogisticated air and common air, in the same proportions as before; and the same thing was repeated on January 19.

On January 23, the bent tube was, by accident, raised out of one of the glasses of mercury into which it was inverted, by which it was filled with air, and a good deal of the soap-lees were lost; there, however, was enough remaining for examination.

On January 28, and 29, the produce of this experiment was examined in the presence of Sir Joseph Banks, Dr. Blagden, Dr. Dollfuss, Dr. Fordyce, Dr. Heberden, Dr. J. Hunter, Mr. Macie, and Dr. Watson. It appeared that 9290 measures of the mixed air had been forced into the

bent tube from the refervoir *. Besides this, Mr. GILPIN had at different times introduced 872 measures of common air. which makes in all 10162 of air, confifting of 6968 of dephlogisticated air, and 3194 of common air. But as there were 900 measures of air remaining in the tube when the accident happened, the quantity absorbed was only 9262; but this is a much greater quantity that what from my own experiments feemed necessary for this quantity of foap-lees.

The foap-lees were poured into a small glass cup, and the tube washed with a little distilled water, in order that as little as possible might be lost. As they were by this means considerably diluted, they were evaporated to dryness; but it was difficult to estimate the quantity of the saline residuum, as it was mixed with a few particles of mercury.

Some vitriolic acid, dropped on a little of this refiduum, vielded a finell of nitrous acid, the fame as when dropped on nitre phlogisticated by exposure to the fire in a covered crucible; but it was thought less strong. The remainder was diffolved in a small quantity of distilled water, and the following experiments were tried with the folution.

It did not at all discolour paper tinged with the juice of blue flowers.

It left a nauseous taste in the mouth like solutions of mercury, and most other metallic substances.

Paper dipped into it, and dried, burnt with some appearance of deflagration, but not fo strongly or uniformly as when dipped in a folution of nitre. The marks of deflagration, however, were stronger than when the Paper was dipped into a solution

^{*} The method of ascertaining the quantity of air forced in was by weighing the refervoir, as mentioned in the above-mentioned Paper, p. 374. of

of mercury in spirit of nitre, but not so strong as when equal parts of this solution and solution of nitre were used.

A folution of fixed vegetable alkali, dropped into fome of it diluted, produced a flight reddish-brown precipitate, which afterwards assumed a greenish colour.

A bit of bright copper being dipped into it, acquired an evident whitish colour, though not so white as when dipped into the solution of mercury in spirit of nitre.

From these experiments it appears, that the mixture of the two airs was actually converted into nitrous acid, only the experiment was continued too long, fo that the quantity of air absorbed was greater than in my experiments, and the acid produced was fufficient, not only to faturate the foap-lees, but also to dissolve some of the mercury. The truth of the latter part is proved by the metallic taste of the residuum, its not discolouring the blue paper, the precipitate formed by the addition of fixed. alkali, and the white colour given to the copper; and the nitrous fumes produced by the addition of oil of vitriol, as well as the manner in which paper impregnated with the refiduum burnt, fhew as plainly, that the acid produced was of the nitrous kind. It is remarkable, however, that during this experiment there were no figns which shewed when the foap-lees became faturated. The only time when the diminution proceeded much flower than usual was on January 4. It then seemed to go on very flowly; but as the air absorbed at that time was only 4830 measures, which is much less than what seems requisite to saturate the alkali, and as the diminution immediately went on again upon adding more common air, it feems not likely, that the foap-lees were faturated at that time.

On January 10, Mr. GILPIN observed a small quantity of whitish sediment on the surface of the mercury; which seems

to shew, that the soap-lees were then saturated, and that the acid was beginning to corrode the mercury. The quantity of air absorbed was also 6840 measures, which is about as much as I expected would be required. However, as I was persuaded, from the event of my own experiments, that the diminution would either intirely cease, or go on very slowly, as soon as the soap-lees were saturated; and as I was unwilling to stop the experiments before that happened, I thought it best to continue the electrification.

On the same morning Mr. GILPIN found, that about 120 measures of the air in the bent tube had been spontaneously absorbed during the night, the quantity therein being so much less than it was the preceding evening, though the electrical machine had not been worked, or any thing done to it during the intermediate time. The reason of this in all probability is, that as the acid was then corroding the mercury, the soaplees became impregnated with nitrous air, which, during the night, united to the dephlogisticated air, and caused the diminution.

Though in reality the event of this experiment was such as to establish the truth of my position, that the mixture of dephlogisticated and phlogisticated air is converted by the electric spark into nitrous acid, as fully as if the experiment had been stopped in proper time; yet, as the event was in some measure different from that of my own experiments, and might afford room for cavil, I was desirous of having it repeated; and as Mr. Gilpin was so obliging as to undertake it again, the materials were, on February 11. put together for a fresh experiment, in the presence of most of the above-mentioned Gentlemen. The soap less employed were the same as before, but 183 measures were now introduced. The dephlogisticated air was different.

different, the former parcel being all used. It was prepared, like the former, from turbith mineral, but was rather purer, as it seemed to contain only $\frac{1}{3\cdot 2}$ of phlogisticated air. The proportion in which it was mixed with common air was that of 22 to 10; so that a greater proportion of common air was now used, in consequence of which it was not necessary for Mr. Gilpin to introduce common air so often.

On February 20, the refervoir was again filled with air of the same kind, in presence of some of the same Gentlemen. As it was found by the last experiment that we must not depend on the faturation of the foap-lees being made known by any alteration in the rate of diminution, the process was stopped as foon as the air absorbed was such as from my own experiments I judged fufficient to neutralize the foap-lees-This was effected on the 15th of March. The air remaining in the tube, when Mr. GILPIN left off working, was 600 measures; but at the time the produce was examined, it was reduced to about 120, fo much having been abforbed without the help of any electrification, which is a still more remarkable instance of spontaneous absorption than what occurred in the former experiment. A few days after the experiment began, a black film was formed in one of the legs, which, I suppose, must have been a mercurial ethiops; but whether owing to some small degree of foulness in the mercury or tube, or to any other cause, I cannot tell. This foulness seemed not to increase; but on March 10, when the air absorbed was about 5200, a whitish sediment began to appear on the surface of the mercury.

On March 19, the produce was examined in the presence of Dr. Blagden, Dr. Dollfuss, Dr. Fordyce, Dr. Heberden, Dr. J. Hunter, Mr. Macie, and Dr. Watson. Vol. LXXVIII.

The mixed air forced into the bent tube from the refervoir was 6650 measures, besides which Mr. GILPIN had at different times introduced 630 of common air, which makes in all 7280, containing 4570 of dephlogisticated, and 2710 of common air.

The foap-lees were evaporated to dryness as before. The residuum weighed two grains, but there were two or three globules of mercury mixed with it, which might very likely weigh half a grain. This being dissolved in a small quantity of water, the following experiments were made with it.

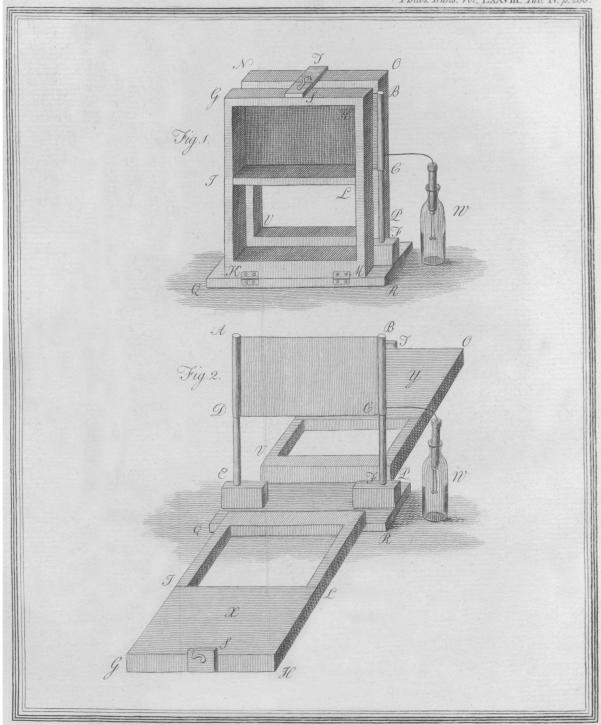
It did not at all discolour paper tinged with blue flowers.

Slips of paper were dipped into it, and dried; and, by way of comparison, other slips of paper were dipped into a solution both of common nitre and phlogisticated nitre, and also dried. The former burnt in the same manner, and with as strong marks of deslagration, as the latter.

It had a strong taste of nitre, but left also a slight metallic taste on the tongue.

It did not give any white colour to a piece of clean copper put into it.

In order to fee whether the whitish sediment, which was before said to be formed in the bent tube, contained any mercury, the remainder of this solution was diluted with some more distilled water, and suffered to stand till the white sediment had subsided. The clear liquor being then poured off, the remainder, containing the sediment, which seemed to amount only to a very small quantity, was put on a piece of bright copper, and dried upon it; a piece of clean gold was then laid over it, and both were exposed to heat. Both metals acquired a whitish colour, especially the gold, but which was very indeterminate.



T: Cavallo del.

In order to discover how nice a test of alcalinity the paper tinged with blue slowers was, a saturated solution of common nitre was mixed with $\frac{r}{120}$ of its bulk of the soap-lees; and this mixture was sound to turn the paper evidently green; so that, as the solution of nitre contains about twice as much alkali as the soap-lees, it appears, that if the residuum had wanted only $\frac{r}{240}$ part of being saturated, it would have discoloured the paper.

From the foregoing trials it appears, that the mixture of dephlogisticated and common air in this experiment was actually converted into nitrous acid, and was sufficient not only to saturate the soap-lees, but also to dissolve some of the mercury. The quantity dissolved, however, was very small, and not sufficient to diminish sensibly the deslagrating quality of the nitre; so that the proof of the air being converted into nitrous acid was as evident as if no mercury had been dissolved.

In this experiment, as well as the former, no indication of the foap-lees becoming faturated was afforded by any ceffation in the diminution of the air; whereas, in my experiments, it was very manifest. I do not know what this difference should be owing to, except to Mr. Gilpin's giving much stronger electrical sparks than I did. In his experiments the metallic knob which received the spark, and conveyed it to the bent tube, was usually placed at about 2½ inches from the conductor, so that the spark jumped through 2½ inches of air, in passing from the conductor to the knob, besides from 1½ to 2½ inches of air in the tube; whereas in my experiments, I believe, the knob was never placed at the distance of more than 1½ inch from the conductor, and the quantity of air in the tube was much less; but the conductor and electrical machine were the same.

Except this, the only difference I know in the manner of conducting the experiment is, first, that Mr. Gilpin usually continued working the machine for half an hour at a time, whereas I seldom worked it more than ten minutes; and, secondly, that in Mr. Gilpin's Experiments the common air in the reservoir bore a less proportion to the dephlogisticated air than in mine; in consequence of which it was necessary for him frequently to introduce common air. On this account, the proportion of the two airs in the bent tube would be considerably different at different times; but on the whole, the common air absorbed bore a greater proportion to the dephlogisticated than in mine.

Though the whole quantity of air absorbed in these experiments is known with confiderable precision, yet it is impossible to determine, with any accuracy, how much of each kind was abforbed, on account of our uncertainty about the nature of the air which remained at the end of the experiment. But if in the last experiment we suppose that the air absorbed spontaneously between the 15th and 19th of March was intirely dephlogisticated, and that what remained at the end of that time was of the purity of common air, it will appear, that 4090 of dephlogisticated and 2588 of common air, which is equivalent to 4480 of pure dephlogisticated air and 2108 of phlogisticated air, were abforbed at the time the electrification was stopped, and confequently the dephlogisticated air is $\frac{2}{100} \frac{4}{00}$ of the phlogisticated air; whereas in my first experiment it seemed to be $\frac{2}{1800}$, and in my last $\frac{2}{3}\frac{5}{000}$.

But the quantity of acid produced, and consequently, I suppose, the saturation of the soap-lees, depends only on the quantity of phlogisticated air absorbed; and the effect of the greater or less quantity of dephlogisticated air is only to make the nitre

nitre produced more or less phlogisticated. Now, in this experiment, the bulk of the phlogisticated air was $12\frac{2}{10}$ that of the soap-lees. In my first experiment it was $11\frac{9}{10}$, and in my last $10\frac{8}{10}$.

As many perfons feem to have supposed that the diminution of the air in these experiments is much quicker than it really is, though I do not know any thing in my Paper which should lead to suppose that it was not very flow, it may be proper to fay fomething on this head. As the quickness of the diminution depends so much on the power of the electrical machine, I can only speak as to what happens with the machine used in these experiments. This was one of Mr. NAIRNE's patent machines, the cylinder of which is 12½ inches long, and 7 in diameter. A conductor of 5 feet long, and 6 inches in diameter, was adapted to it, and the ball which received the fpark was placed at two or three inches from another ball, fixed to the end of the conductor. Now, when the machine worked well, Mr. GILPIN supposes he got about two or three hundred sparks a minute, and the diminution of the air during the half hour which he continued working at a time, varied in general from 40 to 120 measures, but was usually greatest when there was most air in the tube, provided the quantity was not fo great as to prevent the spark from passing readily.

The only persons I know of, who have endeavoured to repeat this experiment, are, M. VAN MARUM, assisted by M. PAETS VAN TROOTSWYK; M. LAVOISIER, in conjunction with M. HASSENFRATZ; and M. Monge. I am not acquainted with the method which the three latter Gentlemen employed, and am at a loss to conceive what could prevent such able philosophers from succeeding, except want of patience. But M. VAN MARUM, in his Premiere Continuation des Expériences,

faites par le moyen de la Machine électrique Teylerienne, p. 182. has described the method employed by him and M. VAN TROOTS-WYK. They used a glass tube, the upper end of which was stopped by cork, through which an iron wire was passed, and secured by cement, and the lower end was immerfed into mercury; To that the electric spark passed from the iron wire to the soaplees. After so much of a mixture of five parts of dephlogisticated and three of common air as was equal to twenty-one times the bulk of the foap-lees * was abforbed, fome paper was moistened with the alkali, which by its burning appeared to contain nitre, but shewed that the alkali was not near faturated. The experiment was then continued with the same foap-lees till more of the air, equal to fifty-fix times the bulk of the foap-lees, was abforbed, which is near double the quantity required to faturate them; but yet the diminution went on as fast as ever. It was then tried, by the burning of paper dipped into them, how nearly they were faturated; but they still feemed far from being fo.

The circumstance of using the iron wire appears evidently objectionable, on account of the danger of the iron wire being calcined by the electric spark, and absorbing the dephlogisticated air; and when I sirst read the account, I thought this the most probable cause of the difference in the result of our experiments; but I am now inclined to think that the case was otherwise. From the manner in which M. VAN MARUM expresses himself, it seems that the only circumstance, from which they concluded that the alkali was not saturated, was the impersect marks of deslagration, that the paper dipped into it exhibited in burning; which, as we have seen, might proceed as well from some of the mercury having been dissolved

^{*} This is rather more than half of that requisite to saturate the soap-lees.

as from the alkali not being faturated. I am much inclined to think, therefore, that, so far from the soap-lees not having been faturated, the quantity of acid produced was in reality much more than fufficient for this purpose, and had dissolved a good deal of the mercury; for the quantity of air absorbed favours this opinion, and the phænomena agree well with Mr. GILPIN's first experiment, in which this was certainly the case; whereas, if the diminution had proceeded chiefly from the dephlogisticated air being absorbed by the iron, the tube towards the end of the experiment would have been filled chiefly with phlogisticated air, which would have made the diminution proceed much flower than before; but we are told, that it went on as fast as ever. It is most likely, therefore, that the apparent difagreement between their experiment and mine proceeded only from their having continued the process too long, and from their not having properly examined the produce.

M. VAN MARUM then proceeds to say: "Surpris de cette différence de résultat j'envoyai une description exacte de nos expériences à M. Cavendish, le priant en même tems de m'inftruire s'il pourroit trouver la cause de cette différence; et comme la seule différence essentielle, par laquelle notre expérience différoit de celle de M. Cavendish, consistoit en ce que nous avons employé de l'air pur produit du précipité rouge ou du minium, au lieu de l'air pur produit de la poudre noire formée par l'agitation du mercure avec le plomb, dont M. Cavendish ne donne pas la maniere de le produire *, je le "pria;

^{*} The using the iron wire formed a material difference in our manner of conducting the experiment, and one which may, perhaps, have had great influence on the result; but I do not see how the using some other kind of dephlo-

" priai de me communiquer de quelle maniere il étoit venu a cet air, parceque je desirois de répéter l'expérience avec ce même air: mais comme il ne m'a fourni aucune élucidation fur la cause vraisemblable de la différence du resultat de nos expériences, et qu'il ne lui a pas plu de me communiquer sa maniere de produire l'air pur qu'il avoit employé pour ses expériences, m'écrivant, qu'il s'étoit proposé d'en parler dans un écrit public, la longueur ennuyante de ces expériences nous a fait prendre la resolution de dissérer leur continuation, pour obtenir une parsaite saturation de la lessive, jusqu'à ce que M. CAVENDISH ait publié sa maniere de produire l'air pur, dont il s'es'est servi, nous contentant pour le present d'avoir vu, que l'union du principe d'air pur et de la mosette produit de l'acide initreux, suivant la découverte de M. CAVENDISH."

As I should be forry to be thought to have refused any necessary information to a Gentleman who was desirous to repeat one of my experiments, and who by his situation was able to do it with less trouble than any one else, I hope the Society will indulge me in adding a copy of my answer, that they may judge whether this is in any degree a fair representation of it.

66 TO M. VAN MARUM.

66 S 1 R,

"I received the honour of your letter, in which you inform me of your ill fuccess in trying my experiment on the con-

dephlogisticated air, instead of that prepared from Dr. PRIESTLEY'S black powder, can in the least degree form an essential difference, as in the same paragraph in which I mention my having used this kind of air in my first experiment, I say, that in my second experiment I used air prepared from turbith mineral.

"version of air into nitrous acid by the electric spark. It is very difficult to guess why an experiment does not succeed, unless one is present and sees it tried; but if you intend to repeat the experiment, your best way will be to try it with the same kind of apparatus that I described in that Paper. If you do so, and observe the precautions there mentioned, I flatter myself you will find it succeed. The apparatus you used seems objectionable, on account of the danger of the iron being corroded by absorbing the dephlogisticated air."

"As to the dephlogisticated air procured from the black " powder formed by agitating mercury mixed with lead, as "it was foreign to the subject of the Paper, and as I proposed " to speak of it in another place, I did not describe my me-"thod of procuring it. As far as I can perceive, the fuccess depends intirely on carefully avoiding every thing by which "the powder can absorb fixed air, or become mixed with par-"ticles of an animal or vegetable nature, or any other inflam-" mable matter: for which reason care should be taken not to "change the air in the bottle in which the mercury is shaken, "by breathing into it, as Dr. PRIESTLEY did, or even by " blowing into it with a bellows, as thereby fome of the dust " from the bellows may be blown into it. The method which "I used to change the air was, to suck it out by means of an " air-pump, through a tube which entered into the bottle, " and did not fill up the mouth fo close but what air could " enter in from without, to fupply the place of that drawn " out through the tube.

"I am, &c."

With regard to the main experiment, it was not in my power to give him further information than I did; as I pointed out Vol. LXXVIII.

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the only circumstance to which, at that time, I could attribute the difference in our results. And with regard to the manner of preparing the dephlogisticated air from the black powder, I have mentioned all the particulars in which my manner of proceeding differed from Dr. Priestley's, and have also explained on what I imagine the success intirely depends; so that, I believe, no one at all conversant in this kind of experiments will think that I did not communicate to him my method of procuring that air.

